CURRENT ACTIVITIES AT IITRI ON HIGH-TEMPERATURE PROTECTIVE COATINGS

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By
V. L. Hill
A. L. Hess
M. J. Malatesta

IIT Research Institute
Chicago, Illinois

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INTRODUCTION

This paper summarizes work conducted on Contract NAS7-431, "Protective Coatings in Refractory Metals in Rocket Engines." The technical monitor on this program is Mr. Richard Cannova of the Jet Propulsion Laboratory.

Information described herein summarizes two areas of investigation on the subject contract: (1) development of iridium coatings on tungsten and tantalum, and (2) corrosion rates of refractory materials in flowing fluorine environments. Both of these areas represent developments which are directed toward the use of refractory materials in liquid-fueled rocket engines.

IRIDIUM-SLURRY COATINGS

The use of slurry techniques for developing protective coatings in refractory metals has been studied at IITRI for several years. These studies have resulted in the development of Hf-Ta coatings for tantalum alloys on Contract AF-33-(615)-3071[1] and iridium coatings on the current program. Both of these coatings employ a slurry technique in which a metallic vehicle is employed to provide sintering of the coating. The metallic vehicle is subsequently removed by evaporation to a concentration below the tolerance level for acceptable oxidation behavior. This process enables development of high-melting coating systems at moderate sintering temperature.

The major portion of the efforts on iridium slurry coatings has been devoted to the deposition of iridium on tungsten, using copper as the metallic vehicle, although other substrates and vehicles have been employed. Coatings have been deposited from Ir-Cu slurries containing 10-80 w/o Cu by various inert

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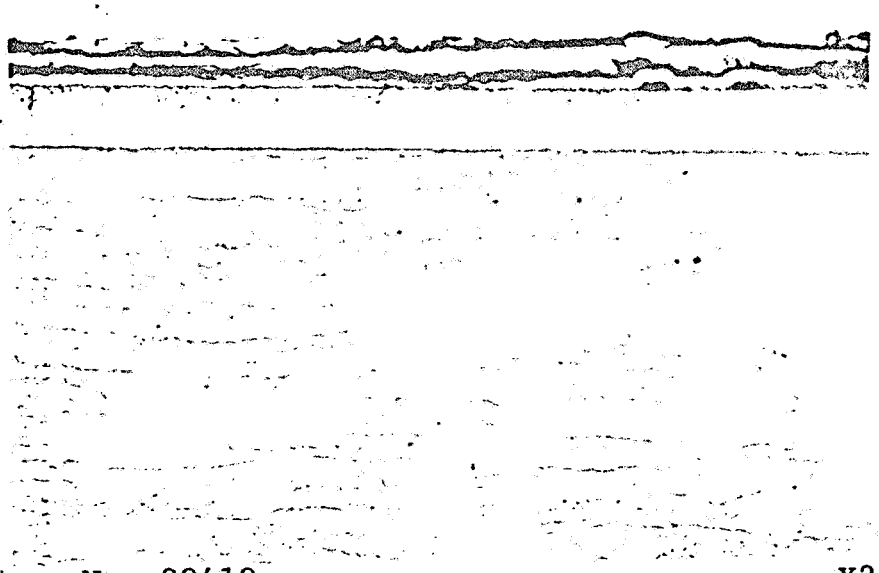
[1] V. L. Hill and J. J. Rausch, "Protective Coatings for Tantalum-Base Alloys," AMFL-TR-64-354, Part III, September, 1966.

atmosphere and vacuum sintering treatments. It was found that slurries containing 30 w/o Cu provide the most uniform coatings on tungsten for sintering temperatures in the range of 2200-2400°F and approximately 3-mil coating thickness. However, the optimum copper concentration is dependent on a variety of factors including: coating thickness, sintering temperature, sintering atmosphere, and, probably, particle size. Coatings of this approximate composition do not flow significantly during sintering so that the final coating thickness is closely related to the original applied coating weight.

The current process for developing iridium coatings on tungsten and rhenium begins with the application of a slurry consisting of Ir-30Cu in an organic vehicle, usually a nitrocellulose lacquer. After air drying, the sample is heat-treated by a combined argon-vacuum cycle at 2200° to 2400°F for about 4 hr. The organic vehicle present after air drying is removed as part of the sintering cycle. Following the lower temperature treatment, the coating is sintered at 3000°F for 1 hr in vacuum to insure maximum density and adherence to the substrate. This treatment normally reduces the residual copper content, as determined by weight loss, below approximately 0.1%. Coatings can be developed on tantalum by a similar technique, except that lower copper contents are required.

The microstructures of iridium coatings on tungsten and tantalum developed from low-copper slurries are shown in Figure 1. Iridium thicknesses shown are in the range of 1 mil, but uniform coatings greater than 3 mils have been deposited on tungsten. The primary difficulty to date in developing coatings thicker than 3.5 mils has been associated with controlling the vaporization of copper to avoid blisters and other defects in the coating. Copper removal rate during the early stages of sintering is the primary parameter which must be controlled to avoid these defects. The removal rate is a function of at least slurry composition, temperature, pressure, coating thickness, and surface area. Control of all of these



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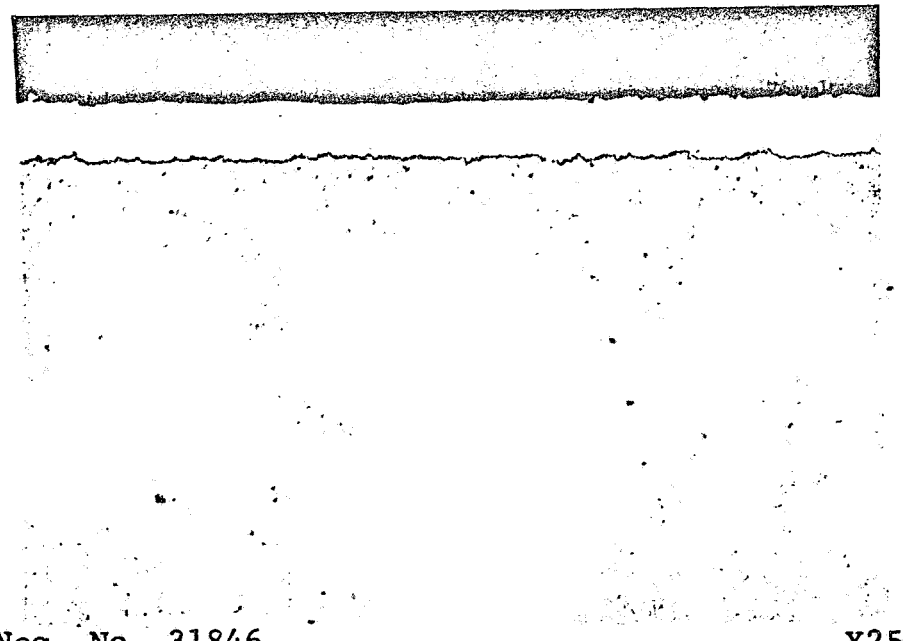
TUNGSTEN



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TANTALUM

FIG. 1 - IRIDIUM SLURRY COATINGS ON TUNGSTEN AND TANTALUM SUBSTRATE.

variables and their interactions is obviously a difficult problem, but they are controllable to the extent that uniform coatings in the range 3-3.5 mils can be obtained. Development of coatings with greater iridium thickness will require additional study of the sintering mechanism.

A limited amount of oxidation testing of iridium-coated tungsten has been conducted in an oxygen-hydrogen torch flame. It is difficult to obtain small test samples which can be uniformly heated because of the hanger which is required during the sintering cycle. Oxidation attack occurs in the hanger area so that weight loss data are inaccurate. The oxidation protection offered by iridium slurry coatings is illustrated in Figure 2. The samples shown were tungsten samples used for sintering studies and, consequently, were only partially coated with approximately 1.5 mils of iridium. These samples were exposed for 2 and 5 min in an oxygen-hydrogen torch flame at 4000°F. The photograph shows complete loss of the 0.125 in. tungsten in 5 min in the uncoated region, although the flame impingement arc was on the lower half of the sample. Some attack of the tungsten beneath the iridium coating occurred at edges, but no spalling of the coating occurred.

Additional data on iridium-slurry coated T-222 with a vapor-deposited tungsten interlayer will be presented by TRW, Inc., on Contract AF-33(615)-5011.

Slurry coating of iridium provides an alternate method to fused salt deposition, vapor deposition, arc-plasma spraying, or other application methods. The advantages of the slurry process include: no basic size limitation, maximum utilization of iridium, and ease of application. The limitation in component size that can be coated is dependent only on the furnace capacity available. Furthermore, since all of the iridium applied in the slurry is retained in the coating and recovery of iridium from the excess Ir-Cu slurry can be readily accomplished by chemical techniques, iridium handling losses are minimal.

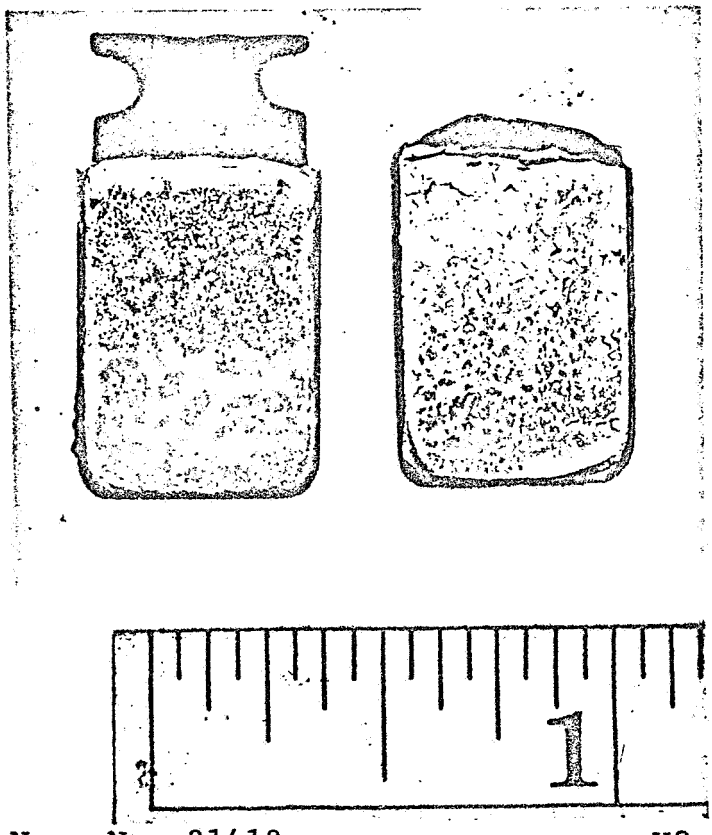

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FIG. 2 - IRIDIUM SLURRY COATINGS ON TUNGSTEN AFTER EXPOSURE AT 4100°F IN AN OXYGEN-HYDROGEN TORCH FLAME FOR 1.5 MIN (LEFT) AND 5 MIN (RIGHT).

An additional advantage of the slurry coating process is that multicomponent coatings can be deposited from a slurry in a single cycle. Iridium coatings containing Hf, Ta, and Re have been produced and the incorporation of other additions, such as other platinum group metals, should be possible. The final structure of the multicomponent coatings is defined uniquely by the phase diagram of the system at the sintering temperature. Consequently, multicomponent solid solution coatings can be developed provided that sintering is conducted in the temperature range over which the single-phase solid solution exists.

Small liquid engine rocket nozzles and inserts have been prepared by slurry coating for firing tests under Contract NAS-7-460. A photograph of a duplex coated Ta-10W nozzle is shown in Figure 3. These components consist of iridium slurry coated tungsten and of iridium-rhenium duplex coated tungsten and Ta-10W. Rhenium was also applied by the slurry process using Cu-Al as the metallic vehicle. The coated surface area is 90-120 cm^2 on these components.

CORROSION OF REFRACTORY MATERIALS IN FLUORINE ENVIRONMENTS

The combustion products of future high-energy liquid propellants will probably contain a high concentration of fluorine compounds. To date, little experimental effort has been devoted to studying the high-temperature corrosion behavior of structural materials in fluorine. Limited work has been done on refractory oxides, carbides, nitrides, borides, and graphite under low flow rate conditions and over limited temperature ranges. The corrosion rates of refractory metals have received little attention. Additional data were required on most refractory materials in order to indicate their corrosion behavior in fluorine environments under high-temperature, high-velocity conditions. The initial corrosion tests were conducted in argon-fluorine mixtures, but subsequent evaluations include HF as the corrosive gas.

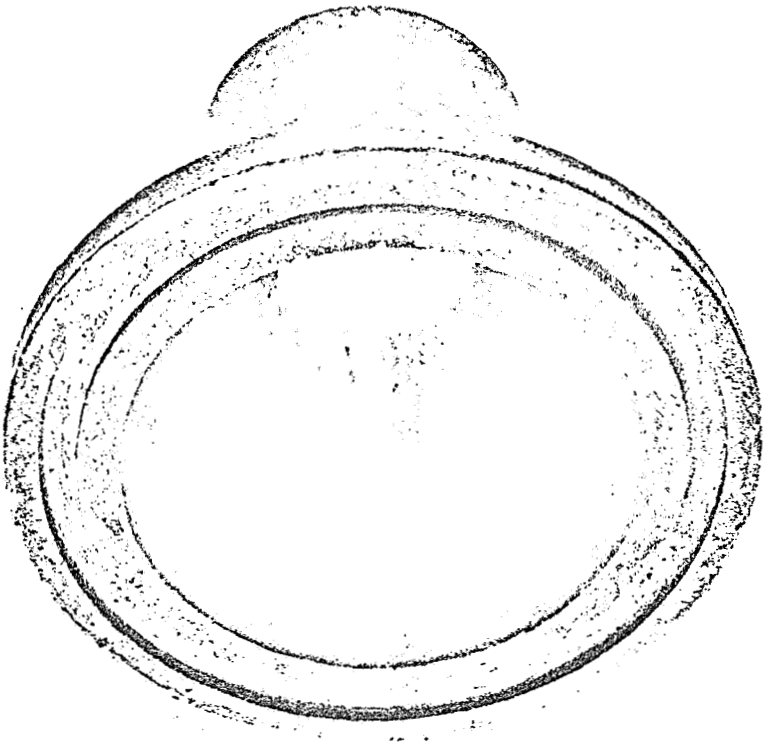

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FIG. 3 - Ta-10W ROCKET NOZZLE AFTER COATING WITH Ir AND Re DUPLEX SLURRY COATING.

A corrosion test facility was constructed allowing determination of the corrosion resistance of structural materials in both HF and F_2 under variable flow conditions. The test facility is shown in Figure 4. Test samples, nominally 0.5 in. x 0.5 in. x 0.125 in. thick, are heated by self-inductance in a thick-walled stainless steel chamber. Thus, the maximum temperature limit is defined by the material under test and input power. Temperature measurements are made optically through a top sight-glass, which permits visual observations of specimen deterioration during testing.

A schematic diagram of the test chamber is shown in Figure 5. Argon and fluorine are metered in precision Pyrex flow meters and are premixed prior to entering the nozzle assembly. Fluorine is passed through a sodium bifluoride trap to remove any residual HF prior to entering the Pyrex fluorine flow meter. Teflon meters are required for HF corrosion tests. This is necessary to eliminate reaction with the fluorine flow meter. The nozzle assembly consists of thick-walled stainless tubing swaged to obtain a 0.036 in. exit nozzle. During testing, the nozzle exit is maintained at a distance of 1 in. from the test specimen. Test specimens are supported in the induction coil by a 0.125 in. tungsten rod, which was split to minimize the contact area and stabilize the test specimen. Reaction products are passed through an activated charcoal absorption column prior to exhaustion through a laboratory hood.

The initial fluorine corrosion tests were conducted with tungsten to obtain reference data and define the operating parameters for the test facility. Fluorine was used initially because it presented fewer handling problems than HF. At first, the flow of the argon-fluorine mixture was maintained during heating to the test temperature. It was found, however, that this technique gave erratic results presumably because of very high corrosion rates at intermediate temperatures for some materials. This effect was apparent although the heating time

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FIG. 4 - EQUIPMENT FOR FLUORINE CORROSION EXPERIMENTS.

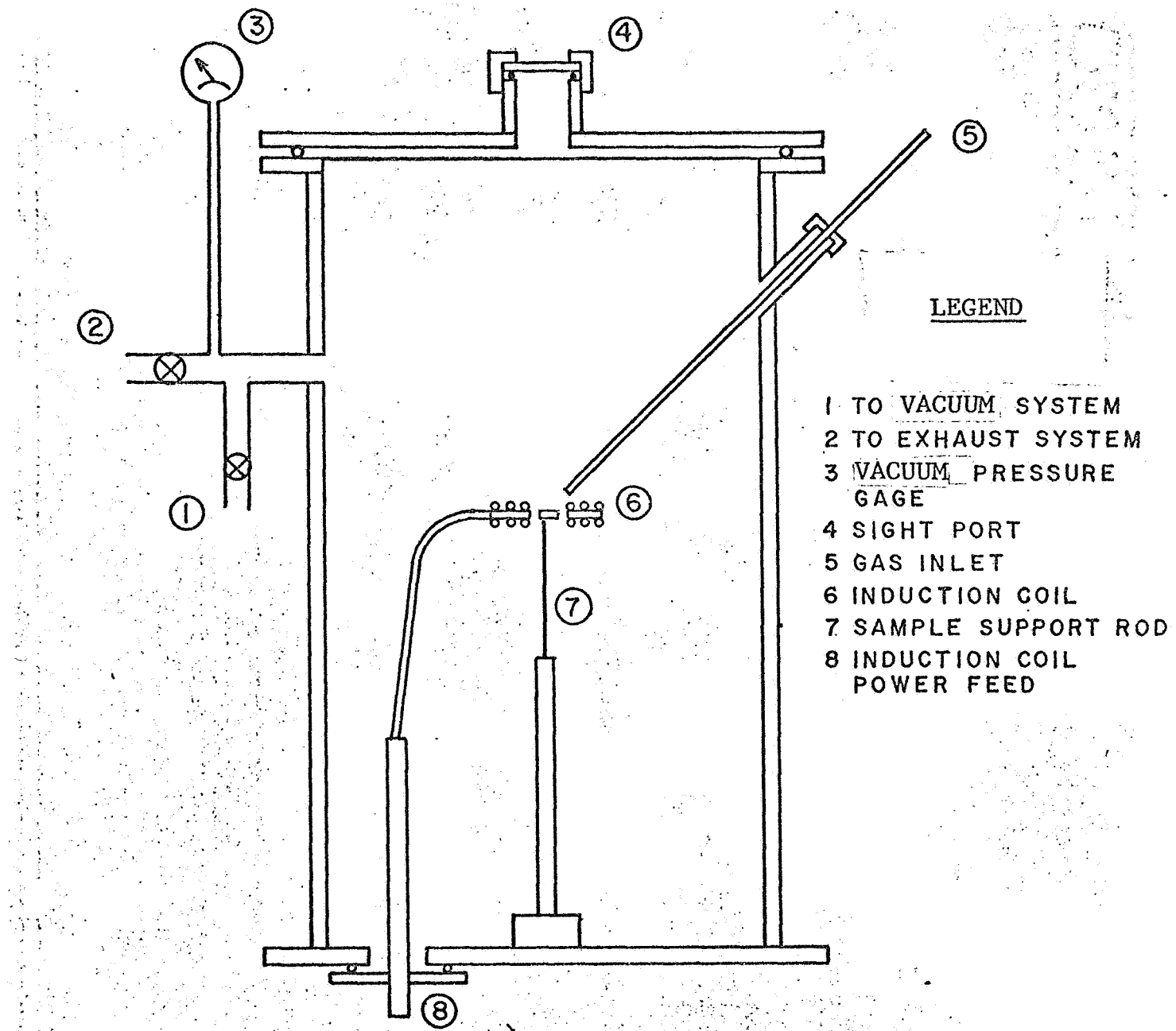

FIG. 5 - SYSTEMATIC DIAGRAM OF FLUORINE REACTION CHAMBER.

through this range was less than 15-30 sec. Subsequently, the testing procedure was modified so that only the argon flow was maintained during heating to the test temperature. After stabilizing at the test temperature, the fluorine flow was started. A minor reduction in temperature ensued, but this could be corrected rapidly. The effect on the measured corrosion rate is minimal, except for very short exposure times. However, this temperature reduction could result in some data scatter, particularly for the materials exhibiting a strong temperature dependence of the corrosion rate.

The selection of materials for the initial fluorine corrosion testing was based on potential substrate and coating materials for nozzle components. Structural materials investigated included tungsten, tantalum, and W-26Re. Metals tested for potential coating systems included iridium, rhenium, and Ir-33Re, since these materials were expected to be the basis for potential duplex coating systems for both oxygen and fluorine environments. JTA graphite was evaluated to compare a graphite-base system with improved oxidation resistance. Subsequently, graphite-carbide composites, borides, and other refractory materials have been investigated.

Test samples for corrosion tests are nominally 0.5 in. x 0.5 in. x 0.125 in. thick. Tungsten, tantalum, iridium, and JTA graphite samples were sectioned from bulk material. Rhenium, Ir-33Re, and W-26Re samples were prepared by cold pressing and sintering -400 mesh powders. The powder compacts were cold pressed at 48 tsi and sintered in a vacuum of 10^{-5} mm Hg at 3500°F for 4 hr. These samples did not attain high density, presumably due to inadequate cold compaction. The density of the rhenium, Ir-33Re, and W-26 Re samples was in the range of 85-90% of the theoretical density. No corrections were applied to the corrosion data for these samples; consequently, the effective surface was slightly greater than that used for corrosion calculations. This results in slightly higher corrosion rate than that which would be measured for high-density material.

A summary of the fluorine corrosion data for selected materials is plotted in Figures 6 and 7. All of the data presented are for a total fluorine plus argon flow rate of 10 cfh, which corresponds to a nozzle exit velocity of approximately 400 fps. The fluorine flow rates used for corrosion testing were 0.04, 0.25, 0.65, and 1.0 cfh. Since the total flow rate was maintained at 10 cfh in all tests, these flow rates correspond to 0.4, 2.5, 6.5, and 10 v/o F_2, respectively. The calculated surface recession rates were based on the original surface area of the sample, including the impingement surface and edges. The bottom surface was not included in these calculations because little or no corrosion was observed on the bottom surface.

The surface recession rates of selected materials in fluorine-argon mixtures at 4000°F are plotted in Figure 6. The rates were calculated from weight loss occurring during a 5 min exposure. All of the materials tested exhibited a linear relationship of corrosion rate with both fluorine concentration and time as would be expected because of the volatile corrosion products formed. Iridium had the lowest corrosion rate; the corrosion rate of iridium was an order of magnitude less than tungsten at all flow rates. Furthermore, the Ir-33 w/o Re alloy corrodes at only a slightly higher rate than that of unalloyed iridium.

The effect of exposure temperature on the corrosion rate in argon-6.5 v/o fluorine is shown in Figure 7. As previously, exposure times were 5 min. Significantly, most of the materials show a decrease in corrosion rate with increasing temperatures. The only exceptions appear to be tantalum and tungsten from 3500° to 4500°F. This is apparently due to a combination of test conditions and a decreasing stability of the corrosion products with increasing temperature. More recent data on tungsten indicate that for the test conditions used (10 cfh total flow rate, 6.5 v/o F_2), the corrosion rate

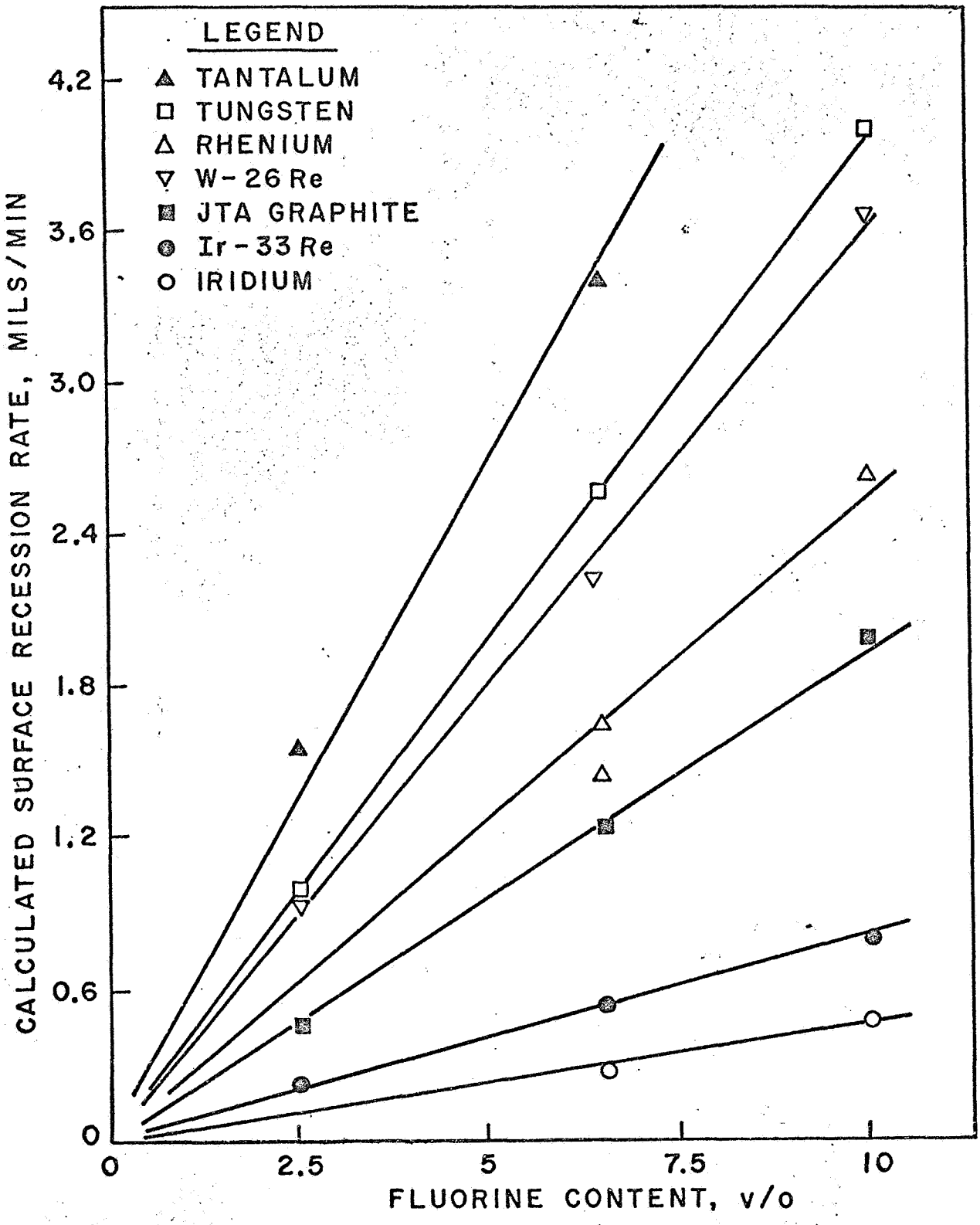

FIG. 6 - CORROSION RATE OF REFRACTORY MATERIALS IN FLOWING ARGON-FLUORINE MIXTURES AT 4000°F.

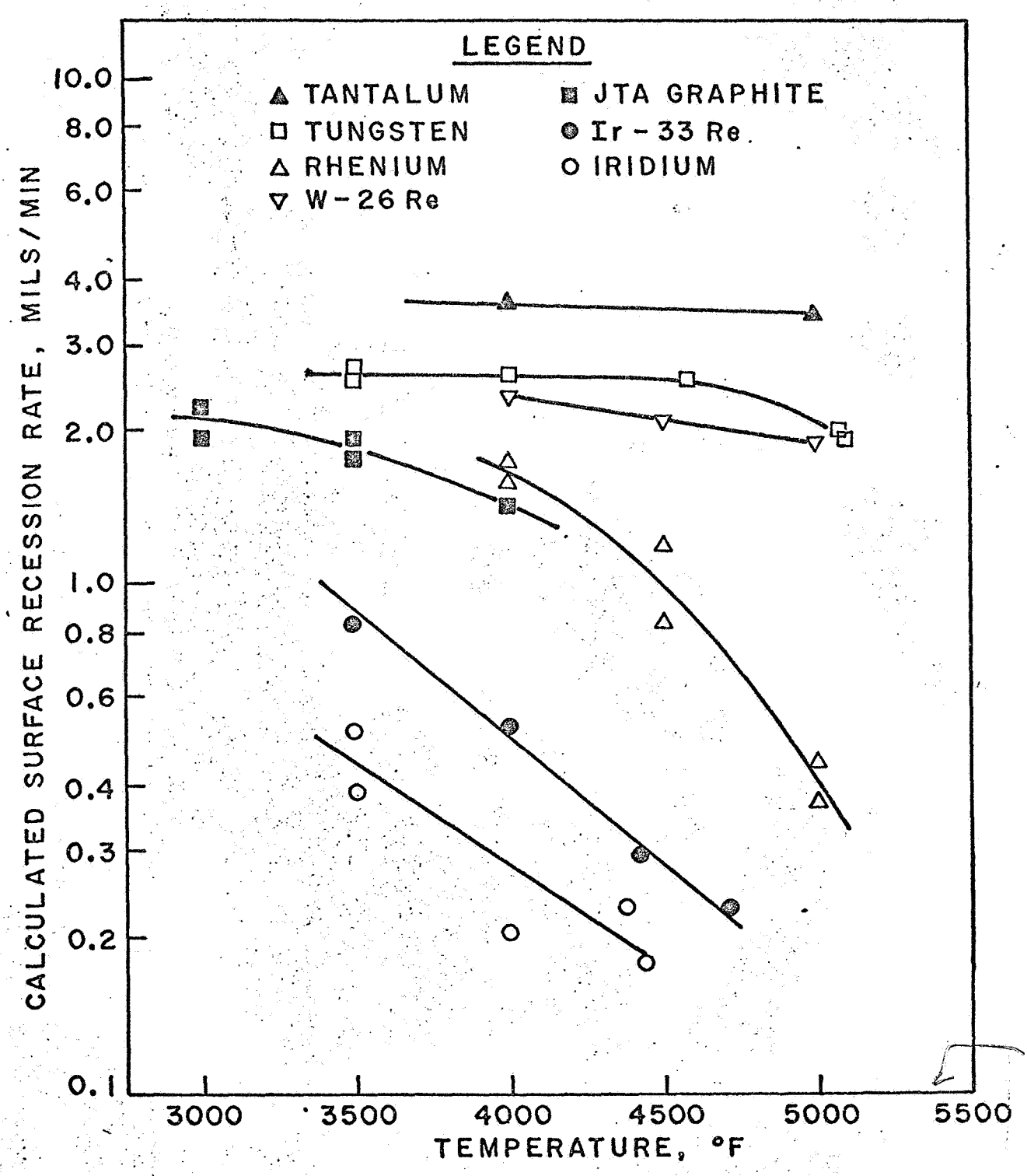

FIG. 7 - CORROSION RATE OF REFRACTORY MATERIALS IN A FLOWING ARGON-6.5 v/o FLUORINE MIXTURE.

increases only slightly in the temperature range of 2200° to 3500°F. Consequently, the test conditions employed for the corrosion tests apparently provide a reaction-controlled corrosion mechanism, and the effect of temperature on the equilibrium between reactants and corrosion products enters into the observed corrosion rate.

Limited study of the corrosion rates of graphite and tungsten in argon-HF mixtures has been conducted. Testing in HF environments is considerably more difficult because of reaction with the Pyrex flow meters and sight glass. Teflon flow meters must be used for HF testing. In addition, HF is a liquid at room temperature and must be heated to supply a gaseous reactant at reasonable flow rates. All of these factors make corrosion testing in HF environments difficult, particularly at higher HF concentrations.

Although the data for HF are probably less accurate than for F_2, the preliminary results indicate that the corrosion rates are considerably less than in F_2. Results to date suggest that the corrosion rate of tungsten in HF is an order of magnitude less than in F_2 at comparable test conditions and fluorine mass flow rates. Similar results were observed with ATJ graphite. However, in contrast to F_2, the corrosion rate of graphite in HF increases with increasing temperature in the range of 2500°-3500°F. This is apparently due to the combined effect of both F_2 and H_2, since the reaction rate of graphite and H_2 becomes significant in this temperature range. The results to date, however, show an order of magnitude decrease in HF corrosion similar to the observed tungsten corrosion rates.

The corrosion rate of iridium slurry coated tungsten in argon-6.5 v/o fluorine at 3500°-4400°F is plotted in Figure 8. Test samples with 3-mil iridium coatings were prepared using the Ir-30Cu slurry previously described. As in oxidation testing, reaction of fluorine with tungsten occurred in the hanger

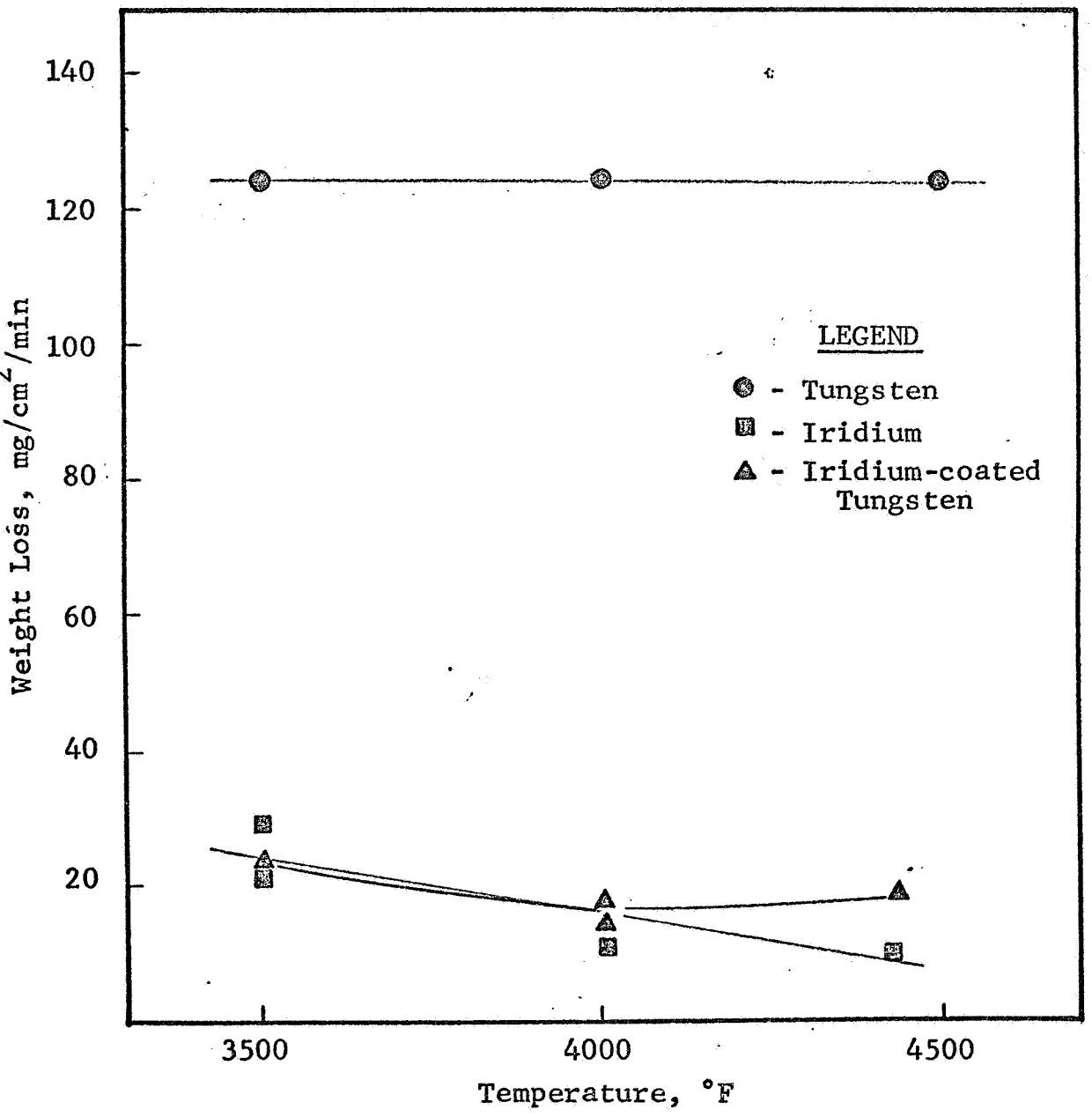

FIG. 8 - CORROSION RATE OF IRIDIUM SLURRY COATED TUNGSTEN IN FLOWING ARGON-6.5 v/o FLUORINE MIXTURES.

area and at defects in the coating. Consequently, the weight loss is due to combined loss of both iridium and tungsten. It is interesting that, although the 4400°F test exceeds the reported Ir-W eutectic temperature (4190°F), rapid deterioration of the system did not occur during the 5 min exposure. Attack of the tungsten substrate did occur at edges, and this is apparently reflected in the higher weight loss at 4450°F.

The fluorine corrosion data described essentially represent a screening test of potential structural and coating materials, since only a limited number of tests were conducted on each material under varying flow conditions. While an increase in corrosion rate with fluorine content was expected, the measured decrease in recession rate with increasing temperature for some materials was not expected. Additional study of the recession rates under wider flow conditions and temperatures is required to fully define the corrosion mechanisms. Further refinement of the testing technique and data analysis is probably also required since the calculation of an average recession rate over the sample does contain inherent errors.

The data obtained for fluorine environments do indicate the potential of Ir-based coatings for both oxygen- and fluorine-containing environments. These coatings, therefore, represent the leading candidates for systems containing both fluorine and oxygen. However, no data exist to date for the corrosion of iridium in combined oxygen-fluorine environments, and the possibility of complex interactions cannot be ignored. Corrosion rate measurements in these environments are required to establish the effect of the combined corrodents. Further evaluation of refractory materials in both F_2 and HF environments is in progress.